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Synthesis and Polymerization of Multiple Aromatic Ether Phthalonitriles

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Multiple aromatic ether-linked phthalonitrile polymers have been synthesized and characterized. The oligomeric monomers are prepared from reaction of an excess amount of a bisphenol such as 4,4′-(hexafluoroisopropylidene)bisphenol or 4,4′-dihydroxybiphenyl with 4,4′-difluorobenzophenone in the presence of either weak or strong bases in *N*-methylpyrrolidinone (NMP) as solvent, followed by end-capping with 4-nitrophthalonitrile. The oligomeric phthalonitrile monomers were cured in the presence of a minute quantity of 1,3-bis(3-aminophenoxy)benzene or *p*-toluenesulfonic acid. The thermal and oxidative properties of two such polymeric systems were compared under identical curing conditions.

Introduction

Intensive investigations of high-temperature polymers in recent decades have led to the development of numerous thermooxidatively stable polymers.[1,2] These materials are usually composed of aromatic/heterocyclic ring systems to achieve thermal and oxidative stability. Full utilization of such polymers has been limited by their brittleness and intractability. Structural modifications such as the incorporation of flexible linkages into the polymeric backbone are necessary to enhance processability without sacrificing thermal stability. Aromatic ether,[3–8] thioether,[9] sulfone,[10,11] and imide[12,13] linkages have been successfully incorporated between terminal phthalonitrile units.

Phthalonitrile-based polymers are a class of high-temperature polymers having a wide range of potential uses such as composite matrices,[14] adhesives,[15] and electrical conductors.[4,5,16,17] Neat polymerization is extremely sluggish, requiring extended heat treatment at elevated temperatures before gelation occurs. Agents that have been used to cure phthalonitrile resins include organic amines,[18] strong organic acids,[19] strong organic acid/amine salts,[20] metallic salts,[21] and metals.[22] Only a minute quantity of curing additive is needed to initiate the polymerization reaction. Various analytical techniques, e.g., NMR[20] and FTIR[23] spectroscopies, have been used in an effort to deduce the nature of the curing reaction. The polymerization reaction occurs through the cyano groups of the phthalonitrile units by an addition mechanism and appears to propagate through multiple reaction pathways involving polytriazine, polyimine, and polyphthalocyanine formations. Recent FTIR and UV studies in our laboratory indicate that phthalocyanine formation is probably a minor product and occurs early in the polymerization reaction before gelation. These heterocyclic cross-linked products are known to exhibit good thermal and oxidative stability. The preferred reaction pathway is probably dependent on the curing agent used. The polymerization rate is easily controlled as a function of the concentration of curing additive and curing temperature, which enhances the importance of the phthalonitrile-based resins as a matrix material for resin transfer molding (RTM). The polymerization reaction can be performed in one step to gelation or can be advanced to any viscosity desired (B-staged) and quenched. The B-staged prepolymer is stable indefinitely under ambient conditions. As a further extension of our work on aromatic ether containing phthalonitrile resins, interconnecting units containing multiple aromatic ether linkages have been incorporated between the terminal phthalonitriles. This paper is concerned with the synthesis and polymerization of such polymers and their characterization by FTIR and thermal analyses.

Experimental Section

Thermal analyses were performed with a duPont 2100 thermal analyzer equipped with a thermogravimetric analyzer (TGA, heating rate 10 °C/min) and a differential scanning calorimeter (DSC, heating rate 10 °C/min) at a flow rate of 50 cm^3/min. Thermal and oxidative studies were achieved in nitrogen and air, respectively. The TGA studies were performed on powdered

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samples. The glass transition temperature (T_g) was reported as the temperature centered at the midpoint between the linear baselines of a DSC scan. The FTIR studies were performed on potassium bromide pellets containing a small amount of sample using a Perkin-Elmer 1800 spectrophotometer. *N*-Methylpyrrolidinone (NMP), dimethylacetamide (DMAC), and 4,4-difluorobenzophenone (**1**) were purchased and used as received from Aldrich. 4,4′-(Hexafluoroisopropylidene)bisphenol (**2A**) was obtained from Hoechst Celanese. 4,4′-Dihydroxybiphenyl (**2A′**) and 4-nitrophthalonitrile (**3**) were procured from Eastman Kodak. 1,3-Bis(3-aminophenoxy)benzene (APB) was acquired from National Starch Corporation.

General Procedure for the Synthesis of Multiple Aromatic Ether Phthalonitrile 4. A series of low molecular weight oligomeric phthalonitriles **4**, in which the average molecular weights were varied by reacting different ratios of an excess of the dialkali salt of bisphenol **2A** or **2A′** with **1** yielding **6** and end-capping with **3**, was prepared. A typical preparation of oligomer **4**, where $N \approx 1$ is as follows: To a 100-mL, three-necked flask equipped with a thermometer and a Dean-Stark trap was added 2.0 g (9.17 mmol) of **1**, 6.2 g (18.35 mmol) of **2A**, and 50 mL of NMP. While stirring to dissolve the two reactants, the solution was purged with dry nitrogen for 30 min. Anhydrous pulverized potassium carbonate (5.0 g, 36.23 mmol) was then added, resulting in discoloration of the mixture to a light pink. The temperature of the reaction mixture was increased to 100 °C and held at this temperature for 1 h. The mixture was then heated to 150 °C, whereupon the Dean-Stark trap was filled with toluene. Toluene (5 mL) was also added to the reaction vessel. The mixture was then refluxed at 170–175 °C for 14 h. The water formed as a byproduct was removed azeotropically. After the toluene was removed by distillation, the reaction mixture was cooled to room temperature, and **3** (3.2 g, 18.4 mmol) was added. The resulting mixture was stirred at 60 °C for 4 h and at 110 °C for 2 h. After cooling, the mixture was poured into 200 mL of dilute HCl, collected by suction filtration, washed with water, and dried to afford 9.1 g (90%) of **4A**.

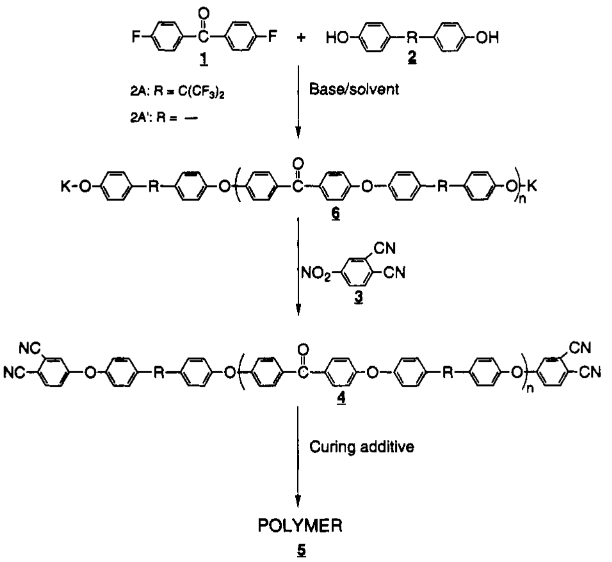
Polymerization of 4A with Aromatic Amine. To the melt of **4A** at 200 °C was added 1,3-bis(3-aminophenoxy)benzene (APB, 2 wt %) with stirring. One minute after the addition, a sample was removed for DSC cure studies. The dark polymerization mixture was cured by heating at 250 °C for 2 h, at 280 °C for 1 h, and at 315 °C for 16 h. The polymer **5A** was postcured at 350 °C for 2 h and at 375 °C for 4 h under oxygen-free argon.

Polymerization of 4A with *p*-Toluenesulfonic Acid (TsOH). To the melt of **4A** at 200 °C was added TsOH (2 wt %) with stirring. One minute after the addition, a sample was removed for DSC cure studies. The sample was cured and postcured in an identical manner as with the amine cure to afford **5B**.

Results and Discussion

As a further extension of our work on aromatic ether containing phthalonitrile resins, our synthetic efforts have produced phthalonitriles **4** of varying average molecular weight containing multiple aromatic ether units[24,25] within the interconnecting linkages between the terminal phthalonitrile units (Scheme 1). The oligomeric phthalonitrile **4** is prepared in situ in one reaction pot. The average length of the oligomeric linkage between the terminal phthalonitrile units depends on the molar ratio of reactants used. Any bisphenol-based compound can be used, ensuring the versatility of the synthetic procedure. In all cases, an excess amount of bisphenol **2** to **1** was used to ensure termination in oligomeric phenolate **6**, followed by end-capping with **3**. The reaction was sluggish in dimethylacetamide (DMAC). Thus, *N*-methylpyrrolidinone (NMP), being a higher boiling solvent, was used to ensure dissolution of the reaction mixture and to simplify the initial displacement reaction involving **1** and **2**. The initial reaction resulting in the formation of **6** can be carried out in the presence of either a weak (potassium carbonate or sodium bicarbonate) or a strong (potassium hydroxide, sodium hydroxide, or lithium hydroxide) base. To ensure a high yield of **6**, the water formed as a byproduct must be removed before the addition of **3**. The water is removed by azeotropic distillation involving toluene. Only enough toluene was added to maintain the refluxed temperature between 145–150 and 170–175 °C when the reaction was carried out in DMAC and NMP, respectively. In all cases, the reaction mixture was refluxed for 14 h. After the toluene was removed by atmospheric distillation, the reaction mixture was cooled to room temperature and **3** was added in one portion.

Scheme 1



The average molecular weight of **4** is dependent on the molar ratios of **1** and **2** used in the initial displacement reaction. A series of low molecular weight phenolates **6** were synthesized from the reaction of an excess amount of either 4,4′-(hexafluoroisopropylidene)bisphenol (**2A**) or 4,4′-dihydroxybiphenyl (**2A′**) and **1**. Oligomeric phthalonitrile **4** is prepared by the displacement of the nitro substituent from **3**, which is activated by cyano groups, by the phenolate **6**. FTIR analysis was used to monitor the extent of the reaction by observing the disappearance of the hydroxyl and nitro absorptions at 3450 and 1539 cm^{-1}, respectively. Figure 1 shows FTIR spectra on films of **4A** for $N \approx 1$, $N \approx 4$, and $N \approx 25$. Below 1600 cm^{-1}, the spectra are basically the same. The main difference is for the absorption attributed to the cyano absorption at 2234 cm^{-1}, which decreases in intensity for $N \approx$ 1–25. A reduction in intensity of the cyano absorption relative to the other characteristic bands is expected as the size of the interconnecting group increases. Phthalonitrile **4** is readily soluble in common chlorinated solvents such as methylene chloride, chloroform, and 1,2-dichloroethane. As the molar ratios were changed to vary the molecular weight from $N \approx 1$ to $N \approx 4$, the ease of processability became more difficult. For $N \approx 1$, the viscosity is very low at 200 °C as determined by the ease of stirring. As the molecular weight is increased or the distance between the terminal phthalonitriles is enhanced, processability becomes more difficult due to an enhancement in the

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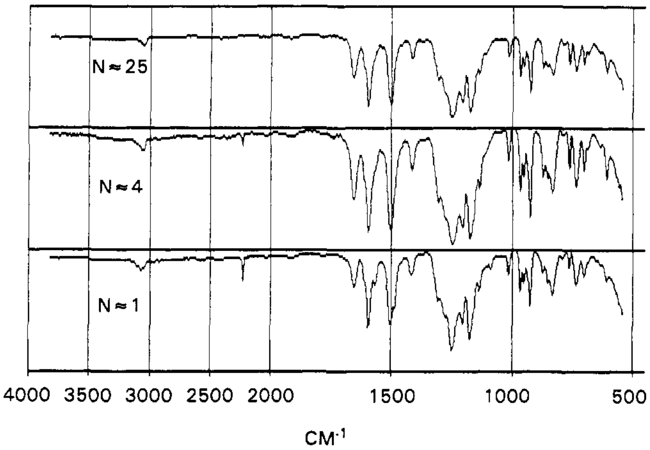
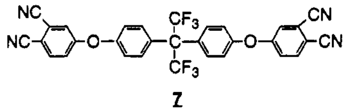


Figure 1. FTIR spectra of oligomeric **4A** for $N \approx 1$, 4, and 25.

viscosity. Moreover, with an increase in molecular weight, 4 is behaving more like a thermoplastic. For $N \approx 25$, oligomeric 4 softens but does not flow at elevated temperatures. Processability involving the addition of a curing additive can be achieved only by blending 4 ($N \approx 25$) with a low molecular weight phthalonitrile such as 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane (7) or 4,4′-(3,4-dicyanophenoxy)biphenyl (8). Phthalonitriles 7



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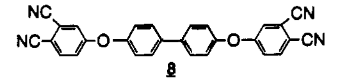

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and 8 behave as reactive plasticizers. As the term implies, the role of the reactive plasticizer is to improve the processability; and then through reaction with 4 and itself, it becomes a part of the cured resin system. Blends of 7 and 8 and oligomeric 4 can be fabricated without seriously compromising the use properties.

Polymerization of **4A** where $N \approx 1$ was achieved by reaction with a small quantity of 1,3-bis(3-aminophenoxy)benzene (APB) and *p*-toluenesulfonic acid (TsOH) to afford **5A** and **5B**, respectively. For the study, 2 weight percent of APB and TsOH was used and the thermal properties of the polymer **5A** and **5B** were compared. Figure 2 shows DSC thermograms of **4A**–APB and **4A**–TsOH mixtures where $N \approx 1$ from 30 to 350 °C of each polymerization mixture sampled 1 min after the addition of curing additives. The thermograms reveal an endothermic transition at approximately 100 °C, corresponding to a glass transition temperature (T_g) and exothermic transitions attributed to the polymerization reaction commencing at approximately 225 and 260 °C for the APB and TsOH mixtures, respectively. DSC thermograms were also obtained on samples that had been cured in air by heating at 250 °C for 2 h, at 280 °C for 1 h, and at 315 °C for 16 h (Figure 3). The **4A**–APB mixture displays endothermic transitions characteristic of T_g's centered at 114 and 240 °C. These transitions may be attributed to competing polymerization reactions. The **4A**–TsOH cured mixture exhibits only one characteristic T_g centered at 260 °C. The higher T_g observed for the TsOH cured mixture suggests that the polymerization reaction proceeds more readily in the acidic medium. After further heating at 350 °C for 2 h and at 375 °C for 4 h, the samples did not exhibit T_g's.

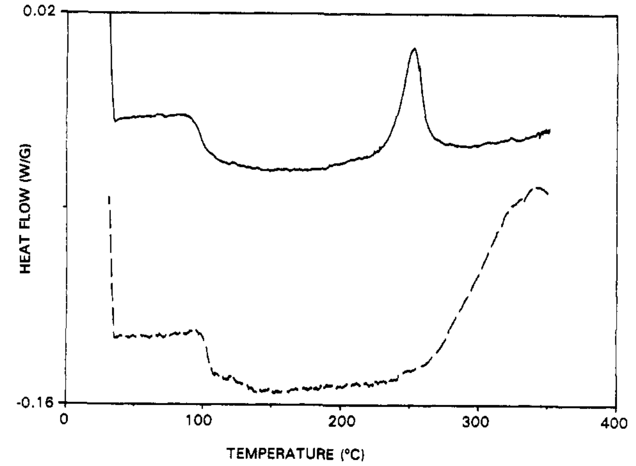

Figure 2. DSC thermograms of: **4A–APB** mixture (solid line) and **4A–TsOH** mixture (dash line).

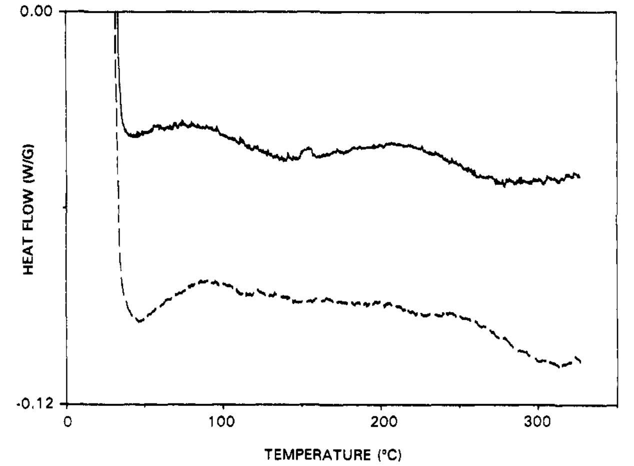

Figure 3. DSC thermograms of polymerization mixtures cured at 250 °C for 2 h, at 280 °C for 1 h, and at 315 °C for 16 h: **5A** (solid line) and **5B** (dash line).

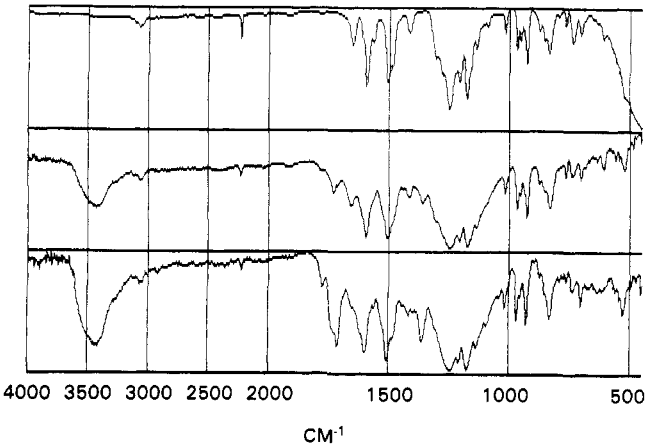

Figure 4. FTIR spectra of **4A** (top), **5A** (middle), and **5B** (bottom).

The polymerization reaction was monitored by infrared spectroscopy (Figure 4). Of primary interest were changes associated with the nitrile absorption centered at 2234 cm^{-1} and the formation of bands that might provide insight into the polymerization mechanism involving the use of a nucleophilic aromatic amine and a strong organic acid as curing additives. When **4A** was cured in air at 250–315

°C, a weak nitrile absorption remained which was more intense for **5A** than for **5B**. This observation indicates that the polymerization reaction proceeds more readily under acidic curing conditions. Moreover, carbonyl bands appeared at 1780 (weak) and 1732 (medium) cm^{-1} and at 1773 (weak) and 1714 (strong) cm^{-1} for **5A** and **5B**, respectively. The bands centered at 1659 (medium) and at 1652 (weak) cm^{-1} in **5A** and **5B** are assigned to C=N absorptions and are probably attributed to polytriazine and polyimine formations.[20,23] An absorption appeared for both polymers centered at 1360 cm^{-1} and was attributed to triazine[23] formation. The 1360-cm^{-1} band was stronger for the TsOH cured sample. Further heating to 375 °C resulted in the disappearance of the nitrile band.

The thermooxidative properties were investigated between 25 and 600 °C. Samples of **5A** and **5B** were compared in relation to the temperature at which the materials commenced to lose weight and catastrophic decomposition occurred. The stability appeared to be dependent on the curing additive and exposure temperature. The oxidative stability was similar for both polymers when cured at a maximum temperature of 315 °C. Polymer **5A** commenced to lose weight at a slightly higher temperature upon postcuring at 375 °C. Surprisingly, **5B** was less stable after heat treatment at 375 °C. Catastrophic degradation occurred in all cases between 500 and 575 °C.

Summary

The synthetic scheme provides a versatile method for obtaining a wide array of molecular weight phthalonitrile 4. The synthesis is a two step, one pot reaction. The overall average molecular weight is controlled as a function of the amount of the reactants, 1 and 2. By variation of the bisphenol 2 used in the synthesis, a new class or series of oligomeric phthalonitrile resins can be realized. The polymerization of the phthalonitrile 4 appears to occur by competing reactions involving polyphthalocyanine, polyimine, and polytriazine formations. Polymerization occurs readily under both amine and acidic curing conditions. Polytriazine formation appears to be more prominent under acidic curing conditions.

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